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Potentially Toxic Elements in Urban Soils: Source Apportionment and Contamination Assessment

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Abstract

Soils play a vital role in the quality of the urban environment and the health of its residents. City soils and street dusts accumulate various contaminants and particularly potentially toxic elements (PTEs) from a variety of human activities. This study investigates the current condition of elemental concentration in the urban soils of Hamedan, the largest and the fastest-growing city in western Iran. Thirty-four composite soil samples were collected from 0-10 cm topsoil of various land-uses in Hamedan city and were analyzed for total concentration of 63 elements by ICP-MS. The possible sources of elemental loadings were verified using multivariate statistical methods (principal component analysis and cluster analysis) and geochemical indices. The spatial variability of the main PTEs were mapped using geographic information system (GIS) technique. The results revealed a concentration for As, Co, Cr, Mn, Mo, Ni and V in the soil samples comparable to the background values as well as a range of associations among these elements in a single component suggesting geogenic sources related to geological and pedogenic processes. Whilst, the soils mostly presented a moderate to considerable enrichment/contamination of Cd, Zn, Pb, and Sb and moderate enrichment/contamination of Cu, Zn and Mo. It was found that anthropogenic factors, vehicular traffic in particular, control the concentration of a spectrum of elements that are typical of human activities, i.e. Cd, Cu, Hg, Pb, Sb and Zn. Lead and Sb were both the most enriched elements in soils with no correlation with land use highlighting general urban emissions over time and the impact of transport networks directly on soil quality. The highest concentrations of As was recorded in the southern part of the city reflecting the influence of metamorphic rocks. The effect of the geological substrate on the Co and Ni contents was confirmed by their maximum concentrations in the city's marginal areas. However, high spatial variability of urban elements' contents displayed the contribution of various human activities. In particular, the increased concentration of Cd, Sb and Pb was found to be consistent with the areas where vehicular traffic is heaviest.

Keywords: *Urban geochemistry; Soil Contamination; Environmental Geochemistry; Multivariate Statistics; Enrichment Factor; Contamination Factor*.

1. Introduction

Urban areas are the most densely-populated areas with the geographical focus of contamination discharging from various anthropogenic sources (Acosta et al. 2009; Pickett et al. 2011; Tume et al. 2018). These sources can include one or more of: transport sources (motor exhausts, brake pads, tire wear); commercial and industrial emissions (energy production, metallurgical industry, electronics, chemical plant, fuel combustion, incinerators, etc.); domestic activities (construction and demolition, waste disposal, wastewater); and agricultural operations (application of fertilizers, pesticides, wastewater irrigation) (Wei and Yang 2010; Patinha et al. 2015; Rate 2018; Argyraki and Kelepertzis 2014; Hu et al. 2013; Li et al. 2017). Emission of harmful substances, in particular Potentially Toxic Elements (PTEs) has become a worldwide environmental concern in urban areas as a result of rapid industrialization and urbanization (Cheng et al. 2014; Johnson and Ander 2008; Manta et al. 2002; Su 2014; Yuan et al. 2014).

Although some elements are essential micronutrients and are considered beneficial for human and plant health and growth, their enrichment may reach levels which become a potential health risk (Fordyce and Ander 2003). In contrast to organic contaminants, PTEs are persistent in the environment and their concentrations remain stable or may accumulate over time (Lee et al. 2006). The prolonged presence of PTEs represents a significant challenge for the health of the urban population (Woszczyk et al. 2018; Micó et al. 2006; Wuana and Okieimen 2011; Guney et al. 2017; Lu et al. 2014; Tang et al. 2013). Direct inhalation, ingestion, dermal contact, drinking of contaminated water and food chain are the principal pathways of human exposure to PTE contaminants in urban environments (Abrahams 2002; McLaughlin et al. 2000; Poggio et al. 2009).

As an essential compartment of the urban ecosystem and sink for PTEs, soils contribute directly or indirectly to the general citizens' quality of life (Biasioli et al. 2006; Christoforidis and Stamatis 2009). Potentially toxic elements from local geogenic sources and from atmospheric deposition of dusts and suspended particles may also be incorporated into urban soil compartment (Norra 2009; Xia et al. 2011). Many researchers have focused on the necessity for a better understanding of urban soil and dust pollution (Hu et al. 2013; Li et al. 2017; Manta et al. 2002). Urban soils are known to have distinctive features such as heterogeneity, high spatial variability of chemical, physical, and biological properties, unpredictable layering, rapid change in land use, poor structure, fragmented distribution and high content of trace elements (Ajmone-Marsan et al. 2010; Kabata-Pendias and Mukherjee 2007; Manta et al. 2002; Xia et al. 2011). For this reason, the traditional approach in environmental survey, used in intact natural environment may not be appropriate in city-wide assessments (Wong et al. 2006). In addition, population, time, location, urban sprawl, intensity of human activities and micro-environmental parameters such as topography, wind direction, and urban runoff may give rise to micro-environmental variation (Amato et al. 2009; Chen et al. 2005).

The characterization of soil and dusts for metal contamination assessment is an effective scientific tool which provides an insight into the source(s) of contamination and enables policy-makers to more effectively manage urban sites in order to protect public and ecosystem health.

This study investigates the geochemistry of urban soils in Hamedan city of Iran where is believed to have an active and increasing pollution burden on its basic infrastructure due to increasing population and industrial growth in previous two decades. The main objectives of this study are: 1) to determine the total concentration of potentially toxic elements (focusing on those with environmental implications) in urban soil under different land uses from Hamedan city; 2) to assess the degree of Hamedan soil pollution in comparison with uncontaminated sub-urban soils and soils from other cities throughout the world as well as applying contamination factor (CF) and enrichment factor (EF); 3) to identify the possible sources (natural and/or anthropogenic) of PTEs in soils and spatial distribution of the accumulated elements.

2. Materials and methods

2.1 Study Area

Hamedan city, in west of Iran (34°48´ N, 48°31´ E), is the official and political center of Hamedan province of Iran. Hamedan is an ancient city with a history of over 3000 years and one of the oldest capitals in the world. Hamedan was the capital city of Median Empire which was conquered in 550 B.C by Cyrus the Great (Jabarivasal 2012). The municipality spreads over an area of about 60 km^2 with a population of about 600,000 according to a national census in 2016. Considering the relative density of population, Hamedan ranks sixth in the country and it is known as a metropolis in February 2010 (Shojaeimehr and Zakerhaghighi, 2013). Hamedan is an important center of economy, transportation and manufacturing. Industrial zones of the city are particularly located at a distance of at least 10km eastward from the city border mainly consisting of small-scale downstream metal industries such as slabs, electrics, car spares, stone polishing etc. Hamedan has experienced a significant urbanization rate during the past 20 years. Considering the ratio of families having cars in the country, it is estimated that Hamedan contains approximately 85000 private vehicles. According to Hamedan news agencies, the local vehicular fleet has increased to more than 4000 public vehicles of which about 390 are public buses and remaining are taxis.

Geographically, Hamedan is located in the northern foothills of the Mt. Alvand at an altitude of 1813 meters above sea level (Shojaeimehr and Zakerhaghighi, 2013). The climate of Hamedan is cold and semi-arid with an average annual rainfall of about 330 mm and a mean temperature of 11°C. The prevailing wind direction is from southeast to northwest.

From the geological point of view, Hamedan is located in the Sanandaj-Sirjan structural zone (SSZ) of the Zagros Mountain Ranges. This area is best characterized by Alvand intrusive complex composed of granite to granodiorite bodies (Fig. 1) outcropped at the surface toward the southwestern side of the city, where Ganjnameh and Abbas-Abad valleys are on view. Metamorphic processes related to Alvand magmatism has produced various facies of slate, phyllite, schist and hornfels rocks which are exposed in the southern part of the city. Hamedan is underlain by the Quaternary alluvial deposits and alluvial fans derived from weathering of the Alvand granitic and metamorphic rocks (Fig. 1).

2.2 Sample Collection and Analytical Methods

Topsoil samples (0–10 cm depth) were randomly collected from all open, unrestricted lands in Hamedan. Samples were taken at 31 locations from residential (8 samples), green spaces (11 samples), agricultural lands (6 samples), parks (4 samples), and playgrounds (2 samples). Four street dust samples were collected from pavements with small plastic brush and pan. In addition, three samples were taken from suburb far from any pollution sources to represent the natural background concentrations. The location of sampling points is shown in Fig. 1. The uppermost topsoil layer is of particular interest in urban geochemistry studies because of the likelihood of atmospheric aerosol deposition from anthropogenic sources. Composite samples were obtained at each sampling site by thoroughly mixing five sub-samples collected at corners and center of a 2×2 m square by using a stainless steel shovel to have a representative sample with a weight of 2kgs. Vegetation debris and coarse-grained particles were manually removed before packing the samples. Soil samples were stored in polyethylene zip-lock bags and transported to laboratory. Soils were dried at room temperature and were then disaggregated to pass through 2 mm nylon sieve mesh for analysis.

The values of pH, EC and TDS were measured using a calibrated instrument in an aqueous suspension of 10g soil and 25ml distilled water according to BS 1377: Part 3:9.0 (1990b) in Zamin Kavan Jonoub Geotechnical Lab, Tehran, Iran.

The organic matter content was measured by Walkley-Black titration method based on the oxidation of organic matter by $K_2Cr_2O_7$ (Sims and Wolf 1995).

The grain size of soil samples was determined by dry sieve analysis based on the particle size distribution procedure provided by BS 1377: Part 2: 9.4 (1990).

The concentration of major and trace elements in soil samples was measured using aqua regia extractions. A 0.5g sample was digested at 90°C in a microprocessor controlled digestion block for 2h. Digested samples were diluted and analyzed for 63 elements by Perkin Elmer Sciex ELAN ICP/MS in ActLabs analytical laboratory, Canada. For quality control and quality assurance purposes, three duplicate and one blank samples were analyzed. The analytical data represents reasonable and good precision mostly less than 8% and never higher than 10%.

2.3 Statistical Methods

The geochemical results were analyzed for descriptive and multivariate statistics using R3.3.1 and SPSS 23.0 software. First of all, the distribution of data was tested with the Shapiro-Wilk's test ($p<0.05$). Due to the non-normal distribution of the data, nonparametric statistics was used. Nonparametric kruskal-wallis test was conducted to determine the differences of PTEs concentration among the five different land uses. The degree of correlation between the measured elements was determined with Spearman correlation matrix ($p<0.05$, $p<0.01$). Additionally, principal component analysis (PCA) was employed to elucidate the possible sources of PTEs in the Hamedan surface soils. In the PCA, different groups of elements were categorized based on the concept of communality for each element. PCA is a powerful tool to differentiate pollution. The varimax rotation method was used in this analysis to improve the value of factor matrix. Hierarchical cluster analysis (CA) was applied for the same variables to differentiate the geochemical groups using the Ward's linkage method and the results were presented in a dendrogram with Squared Euclidean distances.

2.4 Geochemical Indices

Enrichment factor (EF) is widely used to identify the contribution of anthropogenic sources in soils (Li et al. 2017). EF of individual elements in soils is calculated as:

$$EF=[C_i/C_{Sc}]_{sample}/[C_i/C_{Sc}]_{background}$$

in which:

C_i and C_{Sc} are concentrations of the target and reference element in soil sample and in the background sample. The most commonly used reference elements are Al, Fe, Me, Mn, Sc, Ti (Reimann and Caritat 2000; Yongming et al.

2006). Scandium was preferred to Al and Fe and was selected as the reference element in this study since it has no industrial and/or geogenic origin.

Five levels of enrichment can be categorized on the basis of EF (Qingjie et al. 2008):

- EF<2 deficiency or minimal enrichment,
- 2<EF<5 moderate enrichment,
- 5<EF<20 significant enrichment,
- 20<EF<40 very high enrichment,
- EF>40 extremely high enrichment.

Concentration factor (CF) is the quotient of concentration of each element in soil sample (Cn) and the concentration of the same element in reference soil (Bn) (Dung et al. 2013).

$$CF=Cn/Bn$$

Reference soil can be either the word's mean concentration or determined locally from an unpolluted site. The pollution status of elements is classified into four levels from unpolluted to very polluted as below (Abrahim and Parker 2008):

- CF<1 low contamination;
- 1≤CF<3 moderate contamination;
- 3<CF<6 considerable contamination;
- CF>6 very high contamination

Since the composition of soil samples is varied from site to site, in this study local background values were used to calculate the corresponding degree of EF and CF.

The spatial distribution patterns (geochemical maps) showing the hot spots of elevated concentrations were produced using ArcGIS 10.5 software.

3. Results and Discussion

3.1 Physico-Chemical Parameters

The physico-chemical parameters were determined for Hamedan urban soils. The pH values range from 6 to 7.25 with a mean value of 6.87, which suggest circum-neutral acidity for all the topsoils. Despite the fact that soils of Iran are generally alkaline, the pH of urban soils of Hamedan indicates the influence of the Alvand granite complex. The urban soils of Hamedan have a pH similar to the background with low variation between different land uses.

The electrical conductivity (EC) ranges broadly with a median of 2650µS/cm. The largest EC was measured in residential soils (67300), decreasing in green spaces (EC_{Ave}=5076), parks (EC_{Ave}=2143) and agricultural lands (EC_{Ave}=1938). Playgrounds showed the lowest EC values (EC_{Ave}=1429). The high EC values of soils in residential areas are related to the high calcium content in cement and concrete and gypsum which are commonly found in demolition and construction wastes. Organic matter contents vary from 0.4% to 12.9% with a median of 2.8%. The maximum and the minimum values belong to parks and residential lands, respectively, reflecting active use of soil as a growing medium. Sand is the predominant fraction in 78% of the urban soil samples, showing a silty-sand texture. The rest 22% of the samples show a sandy-silt texture. The soil samples contain 9.89 to 29.9% clay size fraction. Particle size distribution of Hamedan urban soils follows the land use classes of the city.

3.2 PTEs Concentrations

Sixty-three elements were analyzed in all soil samples (Appendix 1); of these, 13 elements were selected for further analysis based on their known significance in the urban environment (Charlesworth et al. 2011; Chen et al. 2005; Giusti 2011; Ljung et al. 2006; Wong et al. 2006; Yesilonis et al. 2008). The mean concentrations of As, Ba, Co, Cr, Mn, Mo, Ni, V and Zn in the soil samples were 18.9, 124, 13.1, 56.4, 683, 0.77, 54.9, 61.1 and 115.2 mg kg^{-1}, respectively. These values were compared to the background values of the elements in soils from remote suburb of Hamedan as well as the mean values of the elements from studies in different cities around the world, as shown in Table 1. It is universally admitted that comparing concentrations of elements in urban soils with values measured in other cities is an advantageous practice to better estimate the status of contamination (Duzgoren-Aydin, 2007).

When compared with the background concentration of the PTEs in the suburban soil of Hamedan, As, showed mean concentrations comparable to the background values, suggesting a geogenic source for this element. Mean concentrations of As in urban and suburban soils of Hamedan are 9 times greater than those in the uncontaminated soils worldwide reported by Kabata-Pendias and Mukherjee (2007). Moreover, it is observed that the content of As measured in urban and background soil samples of Hamedan is above the mean values when compared to 11 other cities around the world. This can be attributed to the natural enrichment of arsenic in Sanandaj-Sirjan plutono-metamorphic belt. Concentrations of Co, Cr, Ni and V in the soils of Hamedan city are below the observed values in suburban areas indicating a geogenic source for these elements. On the other hand, the elements with higher concentration in the urban soil samples compared to the background (e.g. Cd, Cu, Hg, Pb, Sb and Zn) can be possibly connected to certain anthropogenic activities in addition to the original content from the parent soils.

In comparison to the background soil value (0.07 mg kg^{-1}), Cd shows 2 fold rise in urban soils (0.14mg kg^{-1}), though, this is still below the worldwide values for Cd (0.53mg kg^{-1}). In a recent study, Solgi et al. (2016) reported a concentration of 0.23 to 2.30 mg kg^{-1} for Cd in urban park soils of Hamedan. The average content of Cu in Hamedan soils, both city (39mg kg^{-1}) and background (36.5mg kg^{-1}), are greater than those in most of the reported values in other cities. This indicates that in addition to geogenic sources, extra origin(s) from human activities added copper to the urban soils. Similarly, slight increase is observed for the amount of Zn in Hamedan city soils (115mg kg^{-1}) in comparison to the background (90.6mg kg^{-1}) and uncontaminated soils (100mg kg^{-1}) values, suggesting possible anthropogenic sources of Zn in the soils. As can be seen in Table 1, mean concentration of Hg in urban soils is about 11 times higher than the local background levels, representing a significant anthropogenic source for Hg in Hamedan city. Pb and Sb are similarly enriched up to 3 times in the urban soil samples.

The four street dust samples revealed higher concentrations of some PTEs, so that the highest concentration of Cd (0.35mg kg^{-1}) and Hg (1.340mg kg^{-1}) were found in SD17 and the highest content of Mo (1.15mg kg^{-1}) and Pb (289mg kg^{-1}) were measured in SD21 dust samples.

As can be noted from the mean values listed in Table 2, variation in land use showed little effect on distribution of elements in urban soils of Hamedan, confirmed statistically (kruskal-wallis H) that there is no significant difference in concentration of PTEs in various land use types (p-value>0.05). However, it is observed that agricultural land contains high contents of As, Co, Cr, Cu and Ni. Pb and Sb are slightly more concentrated in green space soils. Zn and V are dominant elements in parks and residential areas, respectively.

3.3 Evaluation of the Strength of Soil Pollution

Enrichment factors for PTEs in urban soils of Hamedan are calculated and illustrated in the boxplots Fig. 2.

Almost all of the EF values for As, Co, Cr, Mn, Ni and V in Hamedan soils are below 2 confirming the deficiency or minimal enrichment of these elements and the influence of the local geology. Cadmium has moderately enriched in 32% of the soil samples (2.22<EF<4.84), while 19% of the samples are significantly enriched in Cd (5.23<EF<11.26). The mean EF value for Cd is 3.23. Seven of the 31 analyzed soils fall in the category of "moderate enrichment" for Cu, with the EF values ranging from 2.14 to 3.95. However, the mean value of EF for Cu (1.75) shows “minimal enrichment”. Similar results are shown for Mo with 10 moderately enriched soil samples (32%) and the mean EF value of 1.81. Lead appeared to be the most serious enriched element in soils of Hamedan city with the EF mean value of 6.82. More than half of the soil samples are moderately enriched and 26% are significantly enriched in Pb ($2.59<EF<4.83$ and $5.34<EF<14.44$, respectively). The enrichment of Pb and Cd in Hamedan urban soils has already been identified in previous papers (Solgi et al. 2016; Yeganeh et al. 2012).

Almost all of the analyzed soils (97%), present various levels of enrichment in antimony. 51% of the samples fall into the category of moderate Sb enrichment with the minimum and the maximum observed EF values of 2.04 and 4.62, respectively. Significant enrichment in Sb is observed in 45% of the samples including the EF values ranging from between 5-13.48. One of the samples was very highly Sb enriched, showing the EF value of 22. In average, the enrichment factor of Hamedan soils for Sb is 6.15. Zinc is enriched in 42% of the samples (13 soil samples). Among these, 31% (11 samples) show moderate and the rest show significant enrichments.

Dust street samples including one collected from downtown Shir-Sangi square of Hamedan show the highest EF levels, so that it was extremely enriched showing the EF value of 54.31 for Pb.

The assessment of contamination factor for PTEs of Hamedan urban soils is depicted in Fig. 3. Similar to the results of enrichment factor analysis, the geogenic elements of As, Co, Cr, Mn, Ni and V group together and show the least contamination with the average contamination factor of less than 1. Contamination factor for Cd in about 42% of the samples ranges from 1.2 to 2.9 which indicate moderate contamination for this element. Five of the 31 soil samples with CF values between 3.07 and 3.87 are considerably contaminated by cadmium. For Cu, a moderate contamination is observed in 45% of the samples where the CF ranges between 1 and 2.17. More than half of the samples are moderately contaminated by Mo showing the minimum and maximum CF values of 1.01 and 1.63. The highest contamination factor is observed for Pb and Sb with the same average CF of 3.7. About 58 and 55% of the samples fall in the category of “moderate contamination” for Pb and Sb, respectively. Pb in 26% and Sb in 29% of the analyzed samples are considerably high by showing the respective CF values of 3.15-5.85 and 3.26-4.36. Very high contamination of Pb ($5.49<CF<21.09$) and Sb ($6.13<CF<13.64$) is observed in five and four of the analyzed soil samples, respectively. With respect to Zn, the majority of samples (67%) are within the category of “moderate contamination” and the remaining are low.

The elements with some degrees of enrichment or contamination with respect to the background level probably suggest the influence of human interventions.

3.4 Interrelationship of PTEs

3.4.1. Bivariate statistics

The correlation between the elements can provide some information on their origin in a metropolitan area like Hamedan. Prior to correlation tests, normal distribution of elements was checked by shapiro-wilk test, as correlation coefficient depends on the linear combinations of the variables. The result of Spearman's correlation matrix of the PTEs for the surface soil of Hamedan city is shown in Table 3. As it is indicated, the correlation coefficient between Co and Cr is 0.880, which represents a strong, positive, linear correlation at the 0.01 significance level which shows their close association in most soil samples. In addition, Co shows strong positive correlation with both Ni (0.893) and V (0.717). Cr-Ni and Cr-V form two other highly correlated pairs with a correlation coefficient of 0.836 and 0.766, respectively. In addition, moderately positive correlations are shown between As and Co (0.566), Cr (0.473), Ni (0.526) and V (0.492). As it is mentioned before, As, Co, Cr, Ni and V occur naturally at abundant levels in suburban soils of Hamedan, thus the association of these elements can be a reflection of their common source. Cu-Pb and Pb-Zn show the same considerable positive correlation of 0.825. A significant correlation between Cu with Zn (0.724) was observed due to the coexistence of these elements as a result of human activities in Hamedan city. The element pairs Cd-Zn (0.652), Cu-Hg (0.671), Hg-Pb (0.649), Hg-Sb (0.531), Hg-Zn (0.475) and Ni-V (0.532) had high to moderate positive linear correlation at 0.01 significance level, indicating the similar influential factor. Pb and Mo (0.433) and Cu and Sb (0.426) were moderately correlated at 0.05 significance level.

3.4.2. Multivariate statistics

In addition to the correlation coefficient analysis, multivariate statistics was used by principal component analysis method for assessment of the sources of PTEs in Hamedan city. Varimax rotation with Kaiser Normalization was applied. Five principal components were extracted from the available dataset accounting for over 80% of the total variance and considering the eigenvalues greater than 1. The results of the factor loading and communalities are shown in Table 4. Factor loadings bigger than 0.71 are regarded as excellent, and those smaller than 0.32 are considered as very poor. The KMO (Kaiser–Meyer–Olkin) test showed a reliable value (0.615) indicating that PTEs concentration data of Hamedan soils are suitable for principal component analysis.

The first factor (F1) explains 28.17% of the total variance and shows positive association between As, Co, Cr, Ni and V with the factor loadings of 0.635, 0.862, 0.814, 0.895, and 0.664, respectively. This factor can be an indication of the influence of lithogenic inputs into the urban soils as the dominant elements are typical lithophile elements according to the Goldschmidt's classification and mineralogical components of rocks in the area. Cr and Ni derived from pedogenic materials are reported from other cities in the world (Zheng et al. 2008; Argyraki and kelepertzis 2014). Association of the major elements of Al (0.844), Fe (0.698), K (0.545), Mg (0.783) confirms a geogenic control and reflects a reasonable grouping based on the similarities in the geochemical behavior of these elements. The basement of Hamedan is composed of pre-Jurassic rocks consisting of schist, hornfels and phyllite (Baharifar et al. 2004; Sepahi 2008). Association of As which is a chalcophile metalloid in F1 group elements, is referred to the Sanandaj-Sirjan plutono -metamorphic belt. This zone of the Zagros Orogen is well-known for As enrichment due to the strong relationship of arsenic with gold mineralization in this particular tectonic settings. This has been reflected in elevated amounts of As in background as well as in the urban soils of Hamedan. Khaleghian and Modabberi, (2014) and Yeganeh et al. (2012) reported the high concentration of As in agricultural soils and potatoes, wheats and Maize grown in agricultural lands around the city. Similar result obtained from urban study of Estarreja, north-western Portuguese coast where high concentration of As in the city soil were attributed to the presence of pyrite in the mineralogical suite of the region (Cachada et al. 2012). Vanadium (0.627) and Fe (0.489) are also partially presented in the second factor (F2, 12.83% of total variance) along with Mn (0.884) and Ti (0.804). The influence of parent material and natural processes is deduced for association of these elements. The third factor (F3) explaining 11.83% of the total variance is dominated by Ba, Cu, Mo and Pb with the factor loading values of 0.712, 0.515, 0.503, 0.831, respectively. The F3 elements, according to many previous studies on urban soil quality, are known as urban elements and are indicators of traffic-related contamination (Adachi and Tainosho 2004; Hays et al. 2011; Rodríguez-Seijo et al. 2017; Saeedi et al. 2012; Zechmeister et al. 2005). These elements contribute in the fabrication of automobiles or as additive for engine operation or fuel or resulting from corrosion and deterioration of vehicle metal parts (Kuang et al. 2004; Dresel 2007). The concentration of Ba, for example, can be related to brake linings in cars and its emission occurs as a result of frictional processes (Fernández–Espinosa and Ternero-Rodríguez 2004). Copper compounds serve as anti-wear additive and friction-reduction agent in lubricants (Okorie et al. 2012). Even though lead used to be a significant component applying as anti-knock agent in petrol (Callender and Rice 2000), it has been phased out from gasoline in 1990s in Iran. Considering the long residence time of Pb and non-biodegradability and cumulative tendency of this element (Mielke et al. 2010), it is believed that enrichment of Pb in current urban soils represents footprints of prevalent use of tetraethyl lead in the past (Carrero et al. 2013;

Cicchella et al. 2008; Dean et al. 2017; Francek 1992; Galušková et al. 2014; Lau and Othman et al. 1997; Lin et al. 1998; MacKinnon et al. 2011; Poňavič et al. 2018; Sutherland et al. 2000; Wong 1982) and its reworking through circulation of urban dusts by local winds. The fourth factor (F4), which accounts for 9.79% of the total variance, is dominated by Cd (0.899), Hg (0.468) and Zn (0.817). The association of these elements can be mainly attributed to transportation means. Vehicle tires are main source for cadmium and zinc which may lead to contamination of urban soils (Davis et al. 2001; Mitchell et al. 2014; Smolders and Degryse 2002; Adachi and Tainosho 2004; Turner and Rice 2010; van Beers and Graedel 2007; van Bohemen and van De Laak 2003; Zheng et al. 2008). Zinc can also be derived from wearable parts on vehicle brakes (e.g. disc pads). Moreover, cadmium is typically an anthropogenic element derived from a wide range of sources in cities including tire wear, paints, pigments, electroplating, plastic stabilizer, solid wastes and wastewaters and phosphate fertilizers (Kisku et al. 2000; Romic and Romic 2003). The association of volatile element of Hg in this PC fits with a model of wider anthropogenic sources in urban environments. Yeganeh et al. (2012) has reported high concentration of Hg in Hamedan soils, water and food crops which has caused significant potential risk for the city population. The exact source of Hg in Hamedan soils is unknown to the authors. Even though copper presented in factor 3, its highest factor loading (0.702) appeared in factor 5 (F5) along with Sb with the factor loading of 0.772. Partial representation of Cu in another factor implies an ambiguous behavior and probably the presence of different anthropogenic inputs. The mean ratio of Cu:Sb which is commonly used to identify the source of antimony, differs significantly in Hamedan soils with the reported diagnostic criteria (Sternbeck et al. 2002) for brake wear particles (4.6±2.3). Therefore, attribution of Sb together with Cu in brake linings is unexpected. Although the particular source of antimony in Hamedan city soils is still not clear, its significant concentration in urban soils compared to the background together with elevated EF and CF values confirm an anthropogenic source for this element. An extra source might be horticulture. As according to Pietrzak and McPhail (2004), this contributes plant macronutrients such as phosphorus in addition to certain metals like copper, as emerged in F5. Factor 6 (F6) explain 9.64% of the total variance and accounts considerable concentration of Mo (0.648). As mentioned before, molybdenum is also weakly presented in F3 displaying its diffuse origin due to the contribution of a wide range of natural and urban parameters (Peltola and Åström 2003).

To illustrate the interrelationship of the elements, the first three factors are plotted in three-dimensional space in Fig. 4, where the associations between elements can be seen.

Cluster analysis was used to visualize the classification of PTEs according to their plausible origin. The dendrograms (Fig. 5) confirm the attributions explained by PCA analysis. Two distinct clusters were identified for the potentially toxic elements in Hamedan urban soils indicating two main sources:

i) Natural: the cluster of geogenic origin which is divided in two subcategories; the upper sub-cluster is made up of V, Ti, K and Mn displaying the geochemical contribution of underlying Alvand batholith. Whilst, the other sub-cluster includes the elements (e.g. Al, Fe, Mg, As, Co, Cr, Ni) which are mainly associated with the metamorphic formations surrounding the Alvand Batholith.

ii) Mixed: in addition to the influence of the local geology in supplying a fraction of trace elements in soil samples, the other extra non-natural sources have loaded certain elements in the studied urban soils of Hamedan. Two sub-clusters were identified with typical anthropogenic elements including Cd, Pb, Zn, Cu, Sb and Hg. As it is found from the bivariate statistical analysis, the concentration of each element presented in the mixed cluster is positively and significantly correlated with the other elements belonging to the same cluster. This fact can be an indication of a common source. The divided components containing Hg-Cd-Zn, Sb-Cu and Ba-Pb-Mo in the PCA analysis is confirmed with the distinct sub-cluster are shown in the CA (Fig. 5). Moreover, as it is explained, anthropogenic elements reveal higher mean concentrations in urban soils compared to the background soils in Hamedan. These evidence along with the calculated elevated values for the enrichment and contamination factors, highlight the input of PTEs from human activities in Hamedan. This group of elements has previously been interpreted as anthropogenic by many scholars (Rodríguez-Seijo et al. 2017; Costa and Jesus-Rydin 2001; Rate 2018).

3.5 Spatial Distribution

The spatial distributions of concentrations of a number of elements in Hamedan city are visualized by a set of geochemical maps (Fig. 6) prepared by ArcGIS. The segment division displayed in the geochemical maps are according to concentrations of 5%, 25%, 75%, 95% and 100%.

In agreement to Spearman, PCA and CA results, the spatial distribution analysis suggests that the concentration of As, Co, Cr, Ni and V is most tightly controlled by soil parent materials. As it is mentioned before, Hamedan is built upon the old alluvial fans and young terraces which are derived from weathering of the metamorphic rocks from short distances in south and southwest of the city. The piedmont alluvial deposits occur along the valley margins toward the Hamedan plain and form the foothills bordered by Alvand metamorphic and plutonic highlands.

In the north, the cultivated land, consists of clay alluvial soils probably originated from metamorphic bedrocks. The development and thickness of sediments increase toward the north.

Concentration of arsenic accords with the metamorphic rock units with the highest values in the southern part of Hamedan city (Fig.6). Toward the north, due to the less influence of metamorphic rocks and continuous leaching process the content of As decreases.

As seen from the maps (Fig. 6), variations in the levels of Co and Ni demonstrate similar pattern where the influence of parent materials has been involved. The total content of Co in the study area is lower compared to Ni, though both elements show hotspots in the city's marginal areas. Despite the fact that Cr displays a spatial distribution different to Co and Ni, the strong statistical correlation among these elements can be attributed to their common natural source.

Two critical regions for Cd are recognized (Fig. 6): the high-value distribution area in north of the city may be related to the agricultural lands and the influence of fertilizers in addition to the impacts of the nearby highway. While, the hotspots in central and southwestern of the urban areas may indicate the direct influence of vehicular traffic. Ganjnameh and Abbas-Abad are roads to recreational and touristic areas in the southwest of the city with significant traffic density. The latter may be the contributing factor in higher concentration of Sb, as a traffic-generated element, appearing in the vicinity of Ganjnameh road. The valley may funneled the wind and prevented dissipation of traffic-related contaminants in the plain. As it is illustrated in the map (Fig. 6), lead is characterized by higher concentrations along the outer ring road of the city which serves both city and regional traffic with constant congestion. This is correlated with traffic volume and association of some infrastructures (garages, auto-truck service and repair shops) which are generally located around the main entrances of the city.

High spatial variability of Cu, Hg, Mo and Zn even in the short range indicates the spatial heterogeneity caused by various human activities (Liu et al. 2014). This is due in part to the natural background soil but, mainly the result of long-term complex anthropogenic processes.

4. Conclusion

Geochemical study of surface soil in Hamedan city of Iran revealed that the concentration of As, Co, Cr, Ni and V are close to the regional background values, so they may have been originated from the natural parent materials. This result is reinforced by correlation coefficients, PCA and CA analyses identifying geochemical association of these elements which were also spatially related. Moreover, the information obtained from this study showed that Pb followed by Sb and Cd are the most enriched elements in Hamedan city soils. These elements along with Cu, Hg, Mo and Zn showed anthropogenic influence mainly related to vehicular traffic and automobile exhaust. It is deduced that the control of industrial activity is minor probably due to the remote location of Hamedan industrial zones (Bou-Ali Industrial Town) in the north of the city at a distance of about 10 km downwind. Land use showed to have little or no effect on the enrichment of PTEs in Hamedan surface soils. Spatial distribution maps displayed the contribution of metamorphic parent rocks in accumulation of arsenic in both natural and city soils. An identical pattern of special distribution was observed for Co, Ni revealing the influence of geogenic factor. In contrast, the urban elements display large variability throughout the city which indicates the interruption caused by human activities. Lead concentration, however, accords with the main highway network of the city inherited from past usage of Pb in gasoline which has been preserved in soils. Due to the traffic density in Hamedan roadways and dense network of roads the potential for ongoing inputs of PTEs exists. The study of bioavailability of concerned elements and their risk assessment is recommended for further research.

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Table Captions

Table 1. PTEs concentrations (mg kg^{-1}) in surface soils of Hamedan city in comparison to Hamedan background soils, uncontaminated soils and the average values in different cities of the world.

Table 2. The result of kruskal-wallis H test and mean values of PTEs (mg kg^{-1}) in 31 soil and street dust samples from various land uses of Hamedan city

Table 3. Spearman's correlation matrix for PTEs in the surface soils and street dusts of Hamedan city

Table 4. The rotated component matrix of PTEs in urban soils from Hamedan

Figure captions

Fig. 1. Geological map of the Hamedan city in West of Iran and the sampling locations (Redrawn from Hamedan 1:100000 scale geological map, Geological Survey of Iran)

Fig. 2. Box plots of PTE enrichment factor (EF) in urban soils of Hamedan; the band near the middle of each box represents the median. The bottom and top of the box are the first and third quartiles, respectively. Whiskers (the vertical lines) are the 1.5 interquartile ranges of the lower and upper quartiles.

Fig. 3. Box plots of PTE contamination factor (CF) in urban soils of Hamedan; the band near the middle of each box represents the median. The bottom and top of the box are the first and third quartiles, respectively. Whiskers (the vertical lines) are the 1.5 interquartile ranges of the lower and upper quartiles.

Fig. 4. Principal component analysis results in the three-dimensional space: plot of loading of the first three factors

Fig.5. Dendrogram of the cluster analysis (CA) of the urban topsoils of Hamedan based on the PTEs concentrations

Fig. 6. Geochemical maps showing the spatial distribution of certain geogenic (As, Co, Ni) and anthropogenic (Cd, Pb, Sb) elements in the urban soils of Hamedan city. The map legends are as per Fig. 1. The diameters of circles are proportional to the concentration of given elements.

Table 1

		As	Cd	Co	Cr	Cu	Hg	Mo	Ni	Pb	Sb	V	Zn
Hamedan Urban soils	Min	11.1	0.01	9.1	42	22.7	0.01	0.48	36.7	17.7	0.57	39	67
	Max	27	0.35	17.1	76	79.3	1.34	1.15	70.6	289	5.25	79	322
	Mean	18.94	0.14	13.08	56.42	39.05	0.15	0.77	54.86	51.77	1.47	61.13	115.16
	Median	18.8	0.11	13.1	58	35.4	0.09	0.72	54	37.9	1.12	62	101
	SD	3.94	0.1	1.97	7.23	13.27	0.23	0.18	9.02	50.43	1.03	10.41	47.21
	Skewness	-.07	.53	-.02	.19	1.65	4.85	.613	.056	3.7	2.41	-.29	3.0
	Kurtosis	-.55	-.82	-.34	.70	2.98	25.46	-.454	-.881	16.8	6.12	-.39	12.0
Hamedan Background soils (mg kg^{-1})		21.9	0.075	18.2	72.5	36.5	0.012	0.7	62.4	13.7	0.39	105	90.6
[1]Uncontaminated soil		2.5	0.53	12	83	24	0.07	1.5	34	44	0.3	67	100
[2]Galway (Ireland)		8		6	35	27			22	58			85
[3]Napoli (Italy)		11.9	0.37	6.3	11.2	74			8.9	141	2		158
[4]Trondheim (Norway)		3.3	0.12		58	32			43	32			80
[5]Annaba (Algeria)			0.3		28.3	23.8				42.3			64.7
[6]Ibadan (Nigeria)		3	0.15		55.5	32			16.5	47			93.5
[7]Murcia (Spain)					16.3	8.9			11.1	21.9			16.6
[8]Baltimore (USA)			0.89		38.3	35.2			18.4	89.3			80.7
[9]Chicago (USA)		13.2		11	65	59			31	198			235
[10]Shanghai (China)			0.52		107.9	59.25			31.14	70.69			301.4
[11]Turku (Finland)			0.2		37	19.15			12.45	20			72.5

[1]Kabata-Pendias (2010), [2]Zhang (2006), [3]Cicchella et al. (2008), [4]Andersson et al. (2010), [5]Maas et al. (2010), [6]Odewande and Abimbola (2008), [7]Acosta et al. (2011), [8]Yesilonis et al. (2008), [9]Cannon and Horton (2009), [10]Shi et al. (2008), [11]Salonen and Korkka-Niemi (2007)

Table 2

Land use	As	Cd	Co	Cr	Cu	Hg	Mn	Mo	Ni	Pb	Sb	V	Zn
AG	21.3	0.1	14.1	62.0	43.1	0.1	663.7	0.7	63.1	49.0	1.6	63.8	107.4
GS	17.3	0.2	12.0	52.5	40.1	0.2	666.0	0.8	49.3	61.5	1.9	57.7	114.6
PK	17.1	0.2	13.5	57.0	38.5	0.1	719.3	0.9	55.0	58.2	1.1	60.8	170.0
PG	17.7	0.1	12.6	54.0	27.4	0.0	610.5	0.6	56.7	25.2	1.4	54.5	88.9
RS	20.8	0.1	13.8	58.0	37.8	0.1	723.8	0.8	55.8	44.0	1.0	65.6	101.0
chi-squared	6.42	6.62	6.19	6.62	3.32	2.54	4.65	7.45	9.77	2.71	3.51	3.00	4.62
df	4	4	4	4	4	4	4	4	4	4	4	4	4
p-value	0.17	0.16	0.19	0.16	0.51	0.64	0.32	0.11	0.04	0.61	0.48	0.56	0.33

Abbreviations: agricultural land (AG), green space (GS), park (PK), playground (PG) and residential (RS)

Table 3

	As	Cd	Co	Cr	Cu	Hg	Mn	Mo	Ni	Pb	Sb	V	Zn
As	1												
Cd	-0.257	1											
Co	.566**	0.088	1										
Cr	.473**	-0.035	.880**	1									
Cu	-0.211	0.3	-0.018	0.201	1								
Hg	-0.003	.386*	-0.016	0.102	.671**	1							
Mn	-0.076	-0.072	.388*	.397*	0.056	0.127	1						
Mo	-0.276	0.006	-.463**	-0.294	.361*	0.261	0.017	1					
Ni	.526**	0.198	.893**	.836**	0.112	0.061	0.115	-.484**	1				
Pb	-0.283	.466**	-0.184	-0.07	.825**	.649**	0.021	.433*	-0.069	1			
Sb	0.127	0.254	-0.016	-0.001	.426*	.531**	0.046	-0.058	0.058	.426*	1		
V	.492**	-0.118	.717**	.766**	-0.078	0.095	.468**	-0.209	.532**	-0.331	-0.105	1	
Zn	-.450*	.652**	-0.127	-0.087	.724**	.475**	-0.073	0.324	-0.026	.825**	.382*	-0.34	1

***. Correlation is significant at the 0.01 level (2-tailed).*

**. Correlation is significant at the 0.05 level (2-tailed).*

Table 4

Elements	Rotated Component Matrix					
	F1	F2	F3	F4	F5	F6
As	**0.635**	-0.042	-0.359	-0.306	-0.009	0.245
Ba	-0.234	-0.075	**0.712**	-0.067	-0.272	-0.171
Cd	-0.065	-0.068	-0.093	**0.899**	0.057	-0.087
Co	**0.862**	0.327	-0.143	0.044	-0.109	-0.234
Cr	**0.814**	0.413	0.194	-0.005	0.073	-0.079
Cu	0.042	0.013	**0.515**	0.169	**0.702**	0.113
Hg	-0.502	0.184	-0.314	**0.468**	0.309	0.066
Mn	0.128	**0.884**	0.087	-0.028	0.023	-0.172
Mo	-0.326	0.032	**0.503**	0.215	0.058	**0.648**
Ni	**0.895**	0.063	-0.132	0.196	-0.003	-0.238
Pb	-0.318	-0.013	**0.831**	0.117	0.171	0.065
Sb	-0.086	0.057	-0.107	-0.007	**0.772**	-0.409
V	**0.664**	**0.627**	-0.225	-0.115	-0.046	0.123
Zn	0.058	-0.089	0.34	**0.817**	0.119	0.051
Al	**0.844**	0.298	-0.221	-0.208	0.008	-0.156
Fe	**0.698**	0.489	-0.175	-0.049	-0.179	-0.312
K	**0.545**	0.447	-0.271	-0.181	0.309	0.376
Mg	**0.783**	0.051	-0.276	-0.015	0.053	0.055
Na	-0.154	-0.025	-0.147	-0.118	0.022	**0.831**
P	0.008	-0.055	-0.116	0.166	**0.77**	0.395
Ti	0.429	**0.804**	-0.088	-0.04	0.022	0.205
Eigenvalue	7.811	2.680	2.241	1.897	1.340	1.263
% variance explained	28.172	12.836	11.834	9.793	9.776	9.644
Cumulative % variance	28.172	41.009	52.843	62.636	72.411	82.055

Extraction Method: Principal Component Analysis.
Rotation Method: Varimax with Kaiser Normalization.
Rotation converged in 9 iterations.

Figure 1.

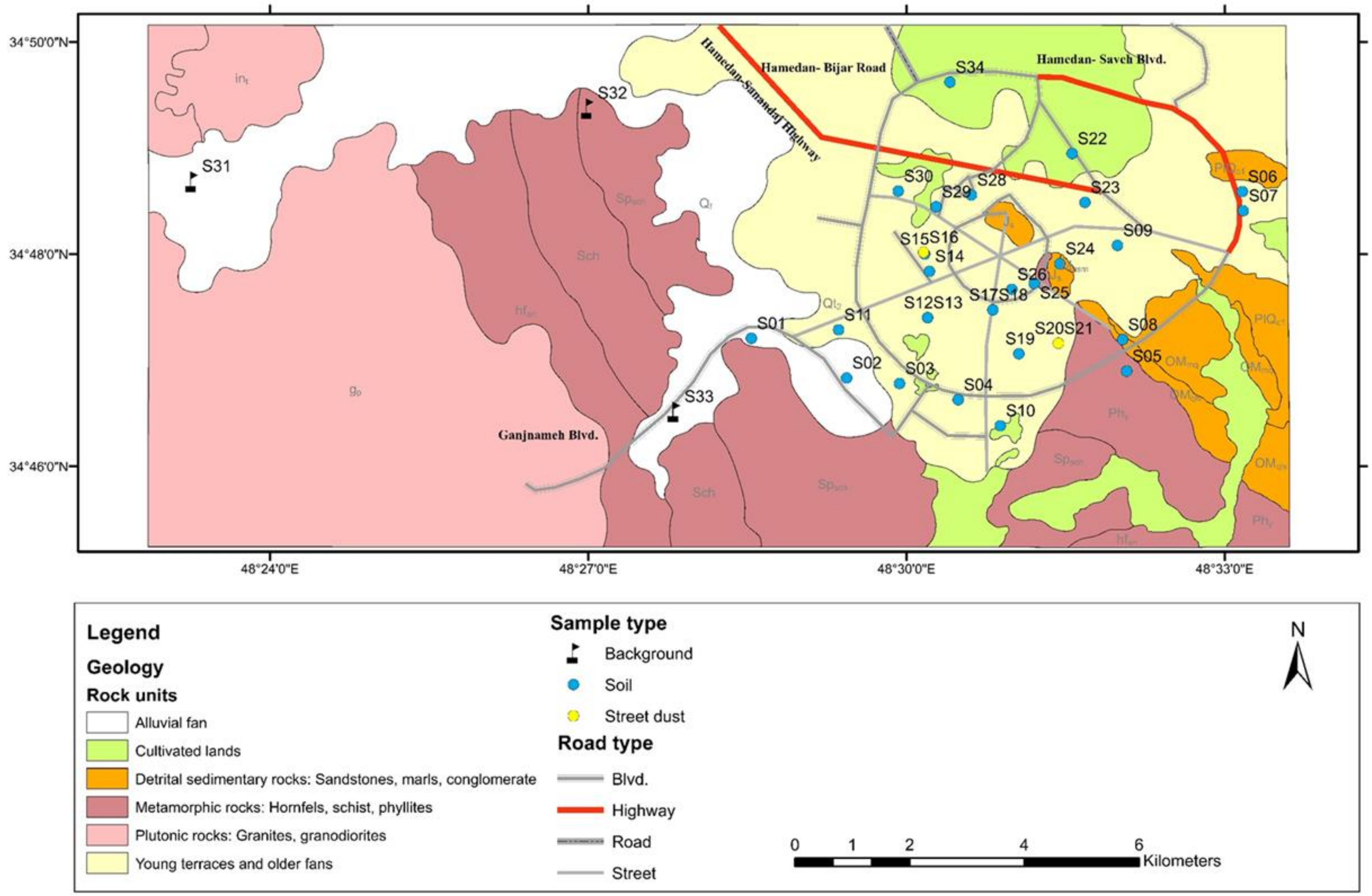
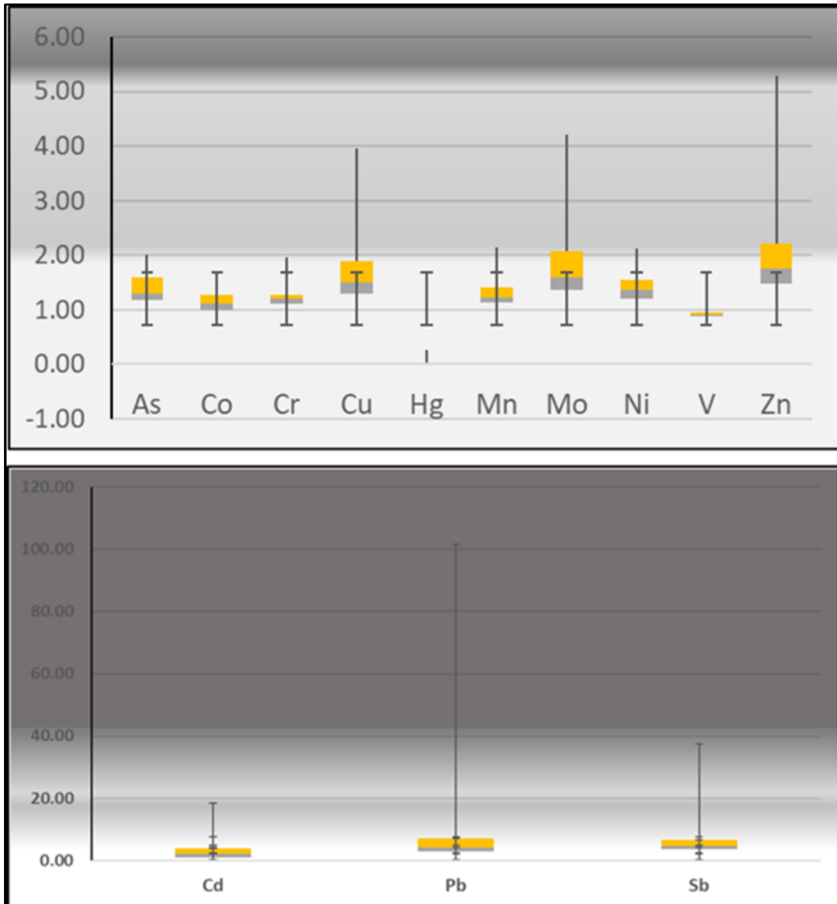
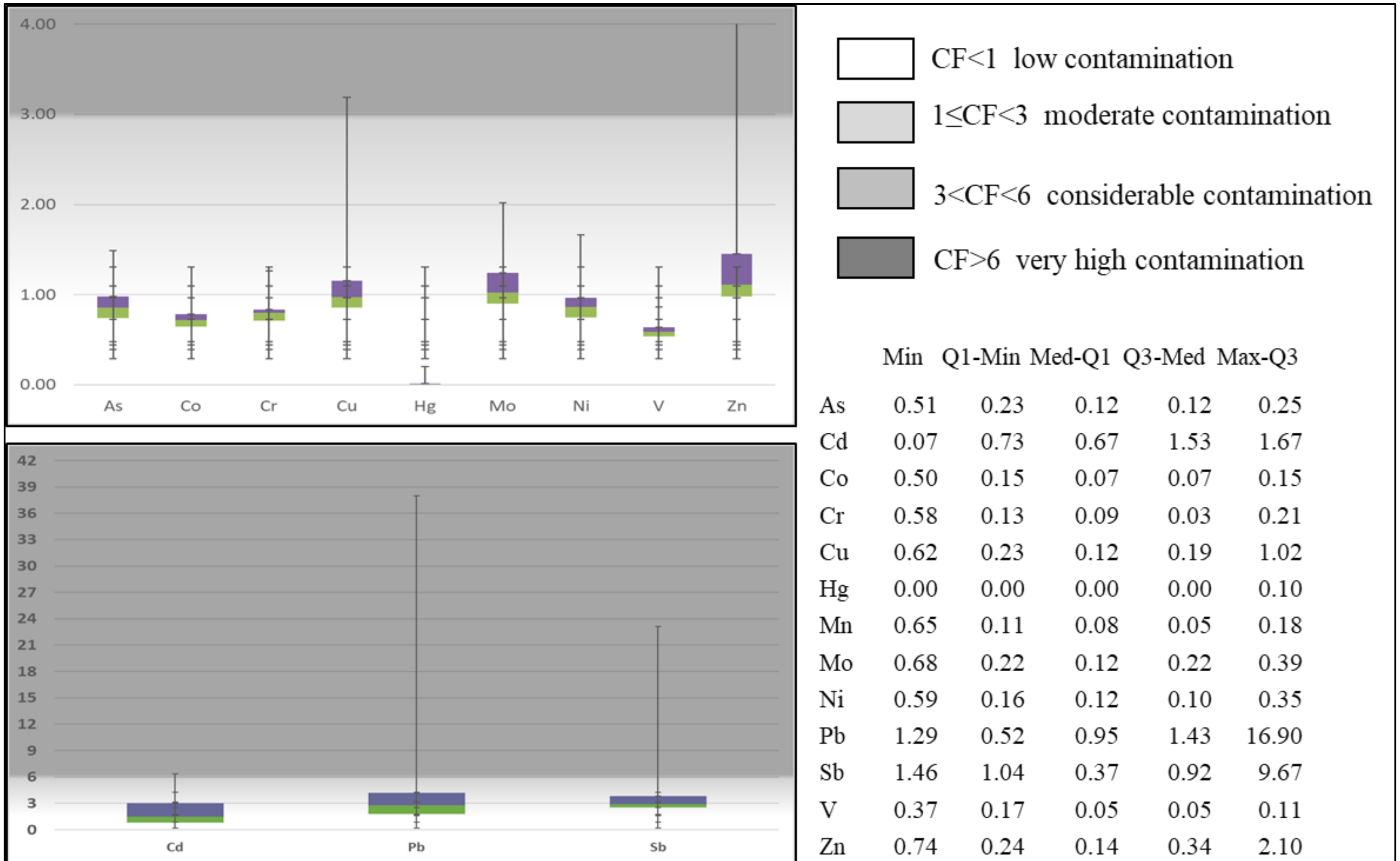

34°50'0"N
34°48'0"N
34°46'0"N
48°24'0"E
48°27'0"E
48°30'0"E
48°33'0"E
Hamedan- Bijar Road
Hamedan- Saveh Blvd.
Hamedan-Sanandaj Highway
Ganjnameh Blvd.
S01
S02
S03
S04
S05
S06
S07
S08
S09
S10
S11
S12
S13
S14
S15
S16
S17
S18
S19
S20
S21
S22
S23
S24
S25
S26
S28
S29
S30
S31
S32
S33
S34
Legend
Geology
Rock units
Alluvial fan
Cultivated lands
Detrital sedimentary rocks: Sandstones, marls, conglomerate
Metamorphic rocks: Hornfels, schist, phyllites
Plutonic rocks: Granites, granodiorites
Young terraces and older fans
Sample type
Background
Soil
Street dust
Road type
Blvd.
Highway
Road
Street
N
0 1 2 4 6
Kilometers

Figure 2.



	Min	Q1-Min	Med-Q1	Q3-Med	Max-Q3
As	0.95	0.22	0.11	0.29	0.41
Cd	0.17	0.93	1.12	1.8	7.24
Co	0.85	0.15	0.12	0.16	0.34
Cr	0.93	0.17	0.11	0.07	0.67
Cu	0.92	0.37	0.22	0.37	2.07
Hg	0.00	0.01	0.00	0.00	0.25
Mn	0.00	1.14	0.08	0.19	0.74
Mo	0.76	0.6	0.25	0.47	2.12
Ni	0.96	0.23	0.16	0.19	0.57
Pb	1.56	1.48	1.16	2.88	47.23
Sb	2.04	1.57	1.01	2.04	15.34
V	0.76	0.12	0.04	0.03	0.26
Zn	0.89	0.59	0.27	0.46	3.06

Figure 3.



	Min	Q1-Min	Med-Q1	Q3-Med	Max-Q3
As	0.51	0.23	0.12	0.12	0.25
Cd	0.07	0.73	0.67	1.53	1.67
Co	0.50	0.15	0.07	0.07	0.15
Cr	0.58	0.13	0.09	0.03	0.21
Cu	0.62	0.23	0.12	0.19	1.02
Hg	0.00	0.00	0.00	0.00	0.10
Mn	0.65	0.11	0.08	0.05	0.18
Mo	0.68	0.22	0.12	0.22	0.39
Ni	0.59	0.16	0.12	0.10	0.35
Pb	1.29	0.52	0.95	1.43	16.90
Sb	1.46	1.04	0.37	0.92	9.67
V	0.37	0.17	0.05	0.05	0.11
Zn	0.74	0.24	0.14	0.34	2.10

Figure 4.

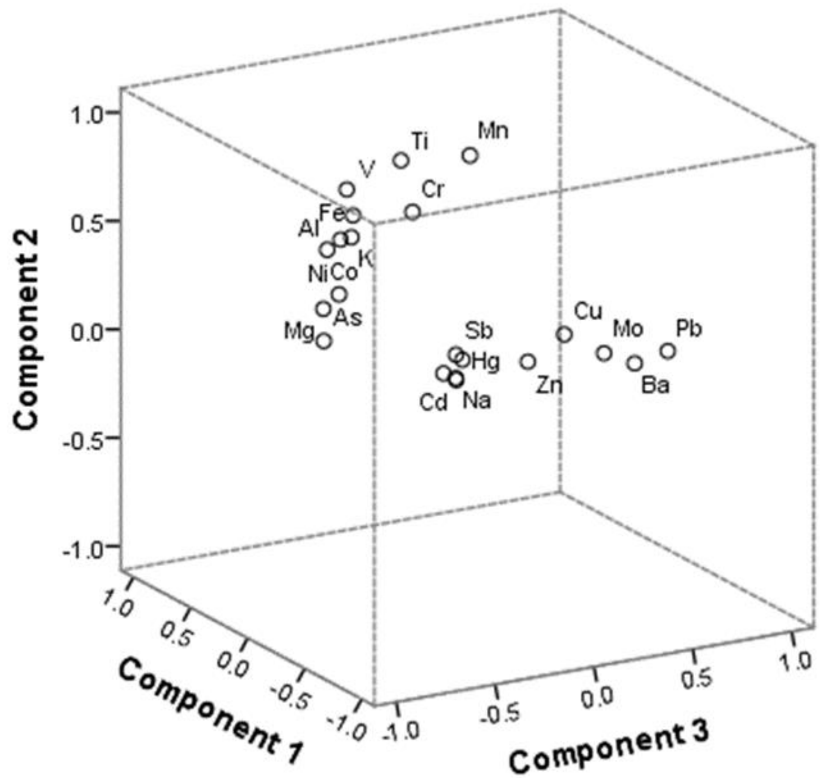

Component 2
1.0
0.5
0.0
-0.5
-1.0
Component 1
1.0
0.5
0.0
-0.5
-1.0
Component 3
-1.0
-0.5
0.0
0.5
1.0
Mn
Ti
V
Cr
Fe
Al
K
Ni
Co
As
Mg
Sb
Hg
Cd
Na
Zn
Cu
Mo
Pb
Ba

Figure 5.

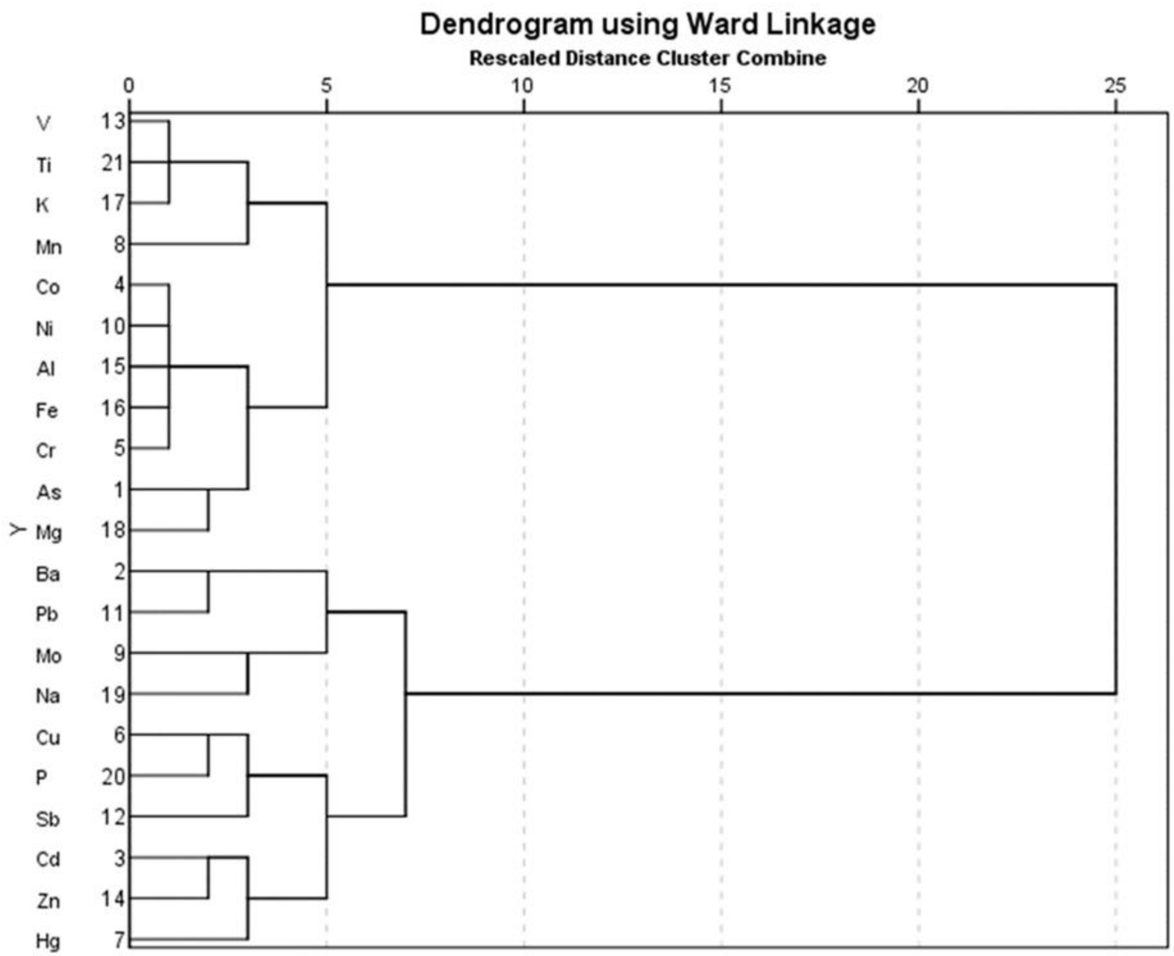
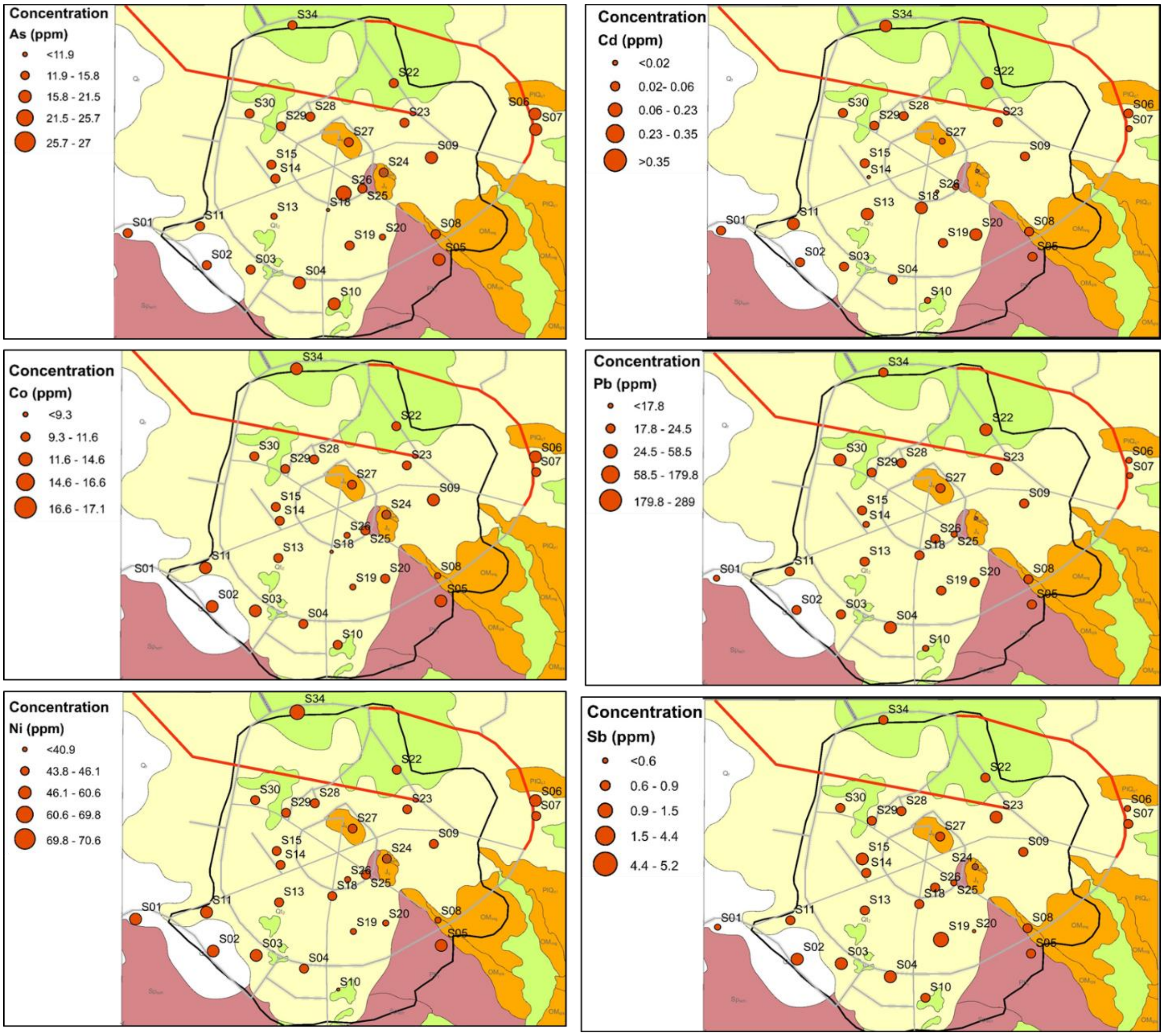

Dendrogram using Ward Linkage
Rescaled Distance Cluster Combine
0
5
10
15
20
25
Y
V 13
Ti 21
K 17
Mn 8
Co 4
Ni 10
Al 15
Fe 16
Cr 5
As 1
Mg 18
Ba 2
Pb 11
Mo 9
Na 19
Cu 6
P 20
Sb 12
Cd 3
Zn 14
Hg 7

Figure 6.


Concentration
As (ppm)
<11.9
11.9 - 15.8
15.8 - 21.5
21.5 - 25.7
25.7 - 27
Concentration
Cd (ppm)
<0.02
0.02- 0.06
0.06 - 0.23
0.23 - 0.35
>0.35
Concentration
Co (ppm)
<9.3
9.3 - 11.6
11.6 - 14.6
14.6 - 16.6
16.6 - 17.1
Concentration
Pb (ppm)
<17.8
17.8 - 24.5
24.5 - 58.5
58.5 - 179.8
179.8 - 289
Concentration
Ni (ppm)
<40.9
43.8 - 46.1
46.1 - 60.6
60.6 - 69.8
69.8 - 70.6
Concentration
Sb (ppm)
<0.6
0.6 - 0.9
0.9 - 1.5
1.5 - 4.4
4.4 - 5.2

Supplementary Material

The results of Sixty-three elements analyzed in urban topsoils of Hamedan

	Unit	Dl	S1	S2	S3	S4	S5	S6	S7	S8	S9	S10	S11	S12	S13	S14	S15	S16	S17	S18	S19	S20	S21	S22	S23	S24	S25	S26	S27	S28	S29	S30	S31	S32	S33	S34
Ti	%	0.001	0.197	0.162	0.123	0.141	0.09	0.088	0.083	0.068	0.122	0.125	0.141	0.1	0.111	0.171	0.113	0.019	0.083	0.074	0.118	0.134	0.071	0.111	0.129	0.179	0.17	0.133	0.129	0.142	0.143	0.134	0.18	0.22	0.331	0.166
S	%	1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1
P	%	0.001	0.114	0.215	0.213	0.329	0.18	0.119	0.129	0.12	0.177	0.118	0.176	0.155	0.248	0.135	0.168	0.086	0.236	0.273	0.232	0.126	0.147	0.135	0.19	0.105	0.115	0.273	0.319	0.176	0.161	0.277	0.132	0.109	0.076	0.289
Li	ppm	0.1	45.7	43.6	38.4	39.8	43.9	38.8	35.5	32.7	41.5	41.4	37.8	31.2	36.2	52.4	35.6	40.4	27.5	28.7	40.5	41.3	24.1	30.7	37.6	55.5	50.1	39.6	36.7	41	34.2	35.9	41.6	44.6	55.8	44.8
Be	ppm	0.1	1.1	1.1	1.1	1.2	1	1.2	1	0.9	1.1	1	1	0.8	1.2	1.2	1	0.9	0.7	0.8	1.3	1	0.9	0.9	0.8	1.3	1.1	1.2	1	1.1	1	0.9	1.6	1	1	1.1
B	ppm	1	16	19	22	20	22	21	23	19	20	14	21	24	27	14	25	10	16	27	18	22	15	16	20	14	14	20	22	22	18	22	10	14	7	21
Na	%	0.001	0.059	0.052	0.049	0.078	0.062	0.058	0.064	0.066	0.084	0.071	0.069	0.137	0.135	0.065	0.066	0.086	0.094	0.092	0.067	0.094	0.078	0.078	0.166	0.07	0.142	0.363	0.128	0.106	0.082	0.075	0.096	0.055	0.057	0.077
Mg	%	0.01	0.94	0.86	0.93	0.93	0.95	0.99	0.83	0.69	0.91	0.68	0.9	0.83	0.92	0.86	0.91	0.71	0.65	0.75	0.77	0.84	0.59	0.77	0.93	0.85	0.85	0.78	0.91	0.87	0.85	0.81	0.72	1.11	1.09	1.1
Al	%	0.01	2.75	2.51	2.4	2.48	2.36	2.49	1.97	1.73	2.25	1.91	2.37	1.73	2.08	2.46	2.14	2.33	1.46	1.55	2.09	1.88	1.41	1.91	2.2	2.29	2.25	2	2.21	2.18	2.08	2.16	2.4	2.92	3.08	2.87
K	%	0.01	1	1.07	0.87	1.04	0.78	0.69	0.65	0.61	0.83	0.77	0.95	0.64	0.89	1.07	0.91	0.58	0.56	0.7	0.85	0.73	0.52	0.69	0.82	0.93	0.87	1.09	1.03	1.16	0.76	0.88	0.77	1.14	1.42	1.23
Bi	ppm	0.02	0.29	0.35	0.34	0.33	0.29	0.24	0.29	0.19	0.28	0.28	0.45	0.23	0.27	0.28	0.24	0.21	0.22	0.26	0.28	0.41	0.23	0.28	0.25	0.25	0.25	0.21	0.25	0.28	0.28	0.42	0.13	0.31	0.39	0.39
Ca	%	0.01	2.41	1.65	5.81	2.59	4.63	6.12	5.53	6.68	5.9	2.27	2.26	4.76	5.7	2.1	4.15	2.92	4.19	4.31	3.24	5.67	4.89	5.35	5.2	4.31	3.04	4.07	4.99	4.32	3.21	3.84	0.91	1.2	0.32	3.69
Sc	ppm	0.1	10.5	9.6	9.2	9.6	7.1	7.5	6.2	5.3	8	7.2	8.5	6.3	7.1	10.9	8	4.9	5.5	4.3	7.4	8	4.7	6.9	7.7	10	9.6	7.9	8.7	8.6	8.1	8.1	9.4	10.3	13.9	10.4
V	ppm	1	79	75	66	67	57	59	53	48	64	61	70	50	57	72	64	45	43	45	57	62	39	56	61	77	69	66	62	67	66	60	71	82	128	78
Cr	ppm	1	67	60	64	63	59	61	50	44	59	48	65	48	58	61	58	50	42	45	54	51	55	53	57	61	55	52	58	60	57	58	50	73	72	76
Mn	ppm	1	883	778	714	765	672	538	625	539	688	603	653	753	691	798	628	593	717	563	662	548	694	699	705	836	789	551	710	681	780	650	661	817	849	690
Fe	%	0.01	4.2	3.82	3.57	3.42	3.54	3.29	3.41	2.81	3.59	3.22	3.66	3.11	3.39	3.77	3.25	3.56	2.84	2.66	3.16	2.98	2.64	3.28	3.37	3.57	3.47	2.91	3.19	3.34	3.3	3.03	3.88	4.12	4.36	3.78
Co	ppm	0.1	17.1	16.2	14.8	13.9	16	14.6	12.8	10.7	14.6	12	14.8	12.6	13.6	14	13.6	11.5	9.5	10.5	11.1	11.6	9.1	12.1	13.6	13.7	12.8	10.6	12.8	13.8	13.1	12.3	14.1	17.7	18.7	16.1
Ni	ppm	0.1	67.3	62.2	68.5	60.6	64.7	69.3	54.8	46.1	60	43.8	67.6	44.2	58.5	54	60.3	53.1	44	47	45.1	45.3	36.7	52.5	59.4	53.7	49.4	44.3	54	59.2	49.6	55	36.9	70.8	54	70.6
Cu	ppm	0.01	31.6	34.8	34.4	40.3	40	29.5	29.4	22.7	35.4	25	46.8	33	40.7	32.4	30.8	24	35.5	38.8	75.5	33.3	56	55.4	52	27.8	27.7	36.4	43.8	39.2	33.3	79.3	25.2	30.2	42.8	45.9
Zn	ppm	0.1	93.4	101	88.3	103	111	87.6	95.3	88.2	106	89	322	134	129	83.5	97.2	80.6	165	170	120	111	146	167	101	67	76.8	69.9	100	102	95.1	134	88.9	85.6	95.6	136
Ga	ppm	0.02	11.1	10.1	9.59	9.93	9.05	8.99	7.66	6.34	8.98	7.98	9.85	6.91	8.05	9.95	8.9	8.01	6.21	6.3	8.62	7.95	5.39	7.53	8.38	9.59	9.4	8.46	8.73	8.88	8.47	8.98	13.5	11.3	13.8	11.4
Ge	ppm	0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1
As	ppm	0.1	20.7	21.2	21.5	24.9	23.2	24.5	22.4	18.1	22.8	23.5	21.4	13.9	15.4	18.8	20.9	14.4	12.8	12.4	15.8	15.1	11.1	17.1	19.4	20.7	17.9	27	18.5	19.7	17.5	16.5	7.8	22.1	21.7	18
Rb	ppm	0.1	68.1	67.7	56.1	62.5	49	45.7	39.4	38.8	52.1	75.9	62	45.6	50.4	72.9	60	26.6	34.2	35.5	62.5	66.2	32.6	41.6	47.2	71.1	65.7	65.9	54	58.2	52.9	57.6	62.2	73	116	74.8
Sr	ppm	0.5	58.1	57	109	80.8	134	175	184	158	135	58.3	75.1	164	156	75.3	117	82.7	141	155	108	145	124	138	158	117	96.5	193	159	124	99.7	112	43.9	35.9	23	121
Y	ppm	0.01	11.9	10.1	9.02	10.2	12.1	10.7	10.2	10.2	11.1	9.35	8.49	12	8.09	10.9	7.79	6.52	10.2	7.2	10.6	7.63	8.98	9.27	10.7	8.52	10.3	7.43	9.26	9.11	10.1	8.48	14.8	9.61	8.13	9.14
Zr	ppm	0.1	2.4	1.4	1.4	1.2	1	1.2	0.8	0.9	1.2	0.9	1.5	0.9	1.1	1.7	1.2	1.7	0.6	1.1	0.7	1.1	0.7	1.1	1.7	2	2	1.3	1.8	1.1	1.5	1.1	2	2.4	2.3	1.4
Nb	ppm	0.1	3.1	2.9	2.5	2.6	1.9	1.7	2.2	1.8	1.9	3	3.6	2.9	3.3	2.2	2.4	0.8	2.5	2.7	3.1	3.9	2.1	1.9	2.1	2.1	2.1	3.2	2.7	3.2	3.4	2.8	2.9	2.8	2.8	3.3
Mo	ppm	0.01	0.7	0.55	0.64	0.57	0.58	0.58	0.66	0.64	0.74	0.87	0.97	0.88	0.86	0.48	0.63	0.55	0.82	0.87	0.67	0.68	1.15	1.12	0.72	0.9	0.76	1.12	0.89	0.71	0.81	1.06	0.48	0.93	0.48	0.58
Ag	ppm	0.002	0.284	0.397	0.484	0.781	0.43	0.289	0.338	0.234	0.651	0.392	0.581	0.323	0.424	0.418	0.46	0.177	1.04	0.543	0.729	0.409	0.328	0.545	0.514	0.282	0.259	0.607	0.749	0.554	0.62	0.892	0.236	0.247	0.144	0.724
In	ppm	0.02	0.05	0.04	0.04	0.04	0.02	0.03	0.03	0.03	0.03	0.03	0.04	0.03	0.03	0.04	0.03	0.03	0.03	0.02	0.03	0.03	0.02	0.03	0.03	0.04	0.04	0.03	0.03	0.03	0.04	0.04	0.05	0.04	0.07	0.04
Sn	ppm	0.05	3.51	5.58	4.87	4.97	16.5	3.18	3.16	2.33	5.29	3.6	7.99	4.18	5.68	4.33	3.29	1.49	4.98	5.58	5.88	5.9	> 200	9.46	5.25	3.56	3.65	6.24	6.37	5.21	4.45	17.6	3.43	2.54	3.62	6.47
Sb	ppm	0.02	0.79	3.62	3.79	1.7	1.27	0.65	1.36	1	1.04	1.37	1.37	0.86	1.01	1.01	2.11	0.73	2.39	1.45	5.25	0.57	1.51	1.36	1.62	0.77	0.63	1.12	0.95	1.05	1.08	1	0.19	0.52	0.26	1.15
Te	ppm	0.02	< 0.02	< 0.02		< 0.02	< 0.02	< 0.02	< 0.02	< 0.02	< 0.02	< 0.02	< 0.02	< 0.02	< 0.02	< 0.02	< 0.02	0.03	< 0.02	< 0.02	< 0.02	< 0.02	< 0.02	< 0.02	< 0.02	< 0.02	< 0.02	< 0.02	< 0.02	0.02	< 0.02	< 0.02	< 0.02	< 0.02	0.03	< 0.02
Cs	ppm	0.02	7.11	8.06	5.59	5.72	5.58	4.55	4.17	4.07	5.37	14.3	6.99	4.08	4.72	6.81	6.14	1.82	3.45	3.15	5.81	6.35	3.02	4.16	4.97	6.41	5.62	12.4	5.05	5.78	6.16	5.43	7.68	7.25	11.2	7.2
Ba	ppm	0.5	127	117	131	114	123	120	105	202	121	103	121	139	128	102	122	115	114	107	99.2	109	219	139	114	118	150	101	114	109	103	116	66.8	134	98.5	133
La	ppm	0.5	29.5	29.1	20.5	25.3	25.9	20.3	19.2	18.1	21.9	25.7	21.7	19.8	17.2	27.1	18.9	26	17.8	14.4	22	17	15.3	18	19.4	16.7	23.3	15.4	18.6	20.3	22.2	21.4	31.4	31.2	37.1	24.6
Ce	ppm	0.01	58.4	56.1	40.6	48.5	51.4	42.2	41.2	37.1	43.8	50.8	42.8	37.2	35.6	52	36.9	50.4	35.4	29.2	43.6	34.1	30.4	35.5	39.5	34.5	46.6	30.7	38.3	41.7	43.6	41.5	60.3	59.5	68.8	48.1
Cd	ppm	0.01	0.07	0.22	0.19	0.15	0.08	0.15	0.06	0.14	0.09	0.05	0.29	0.28	0.23	0.02	0.11	0.03	0.35	0.3	0.09	0.24	0.01	0.35	0.18	0.02	0.06	0.02	0.05	0.19	0.1	0.1	0.07	0.12	0.03	0.24
Pr	ppm	0.1	6.7	6.5	4.7	5.6	5.8	4.8	4.7	4.1	5	5.7	4.9	4.2	4.1	6.1	4.2	5.8	3.9	3.4	4.9	4	3.4	4.1	4.5	3.9	5.3	3.5	4.2	4.8	5	4.7	7	6.8	8.2	5.5
Nd	ppm	0.02	25.4	24.8	17.7	21.9	22.2	17.9	17.3	15.9	18.9	21.9	18.7	16.6	14.7	23	16	22.2	14.5	12.4	18.9	14.8	12.8	15.3	16.7	14.5	19.7	12.7	15.9	17.5	19	18.1	27	26.5	31.6	20.9
Sm	ppm	0.1	4.4	4.2	3.1	3.6	4	3.3	3.1	2.7	3.3	3.8	3.3	2.9	2.7	3.8	2.7	3.6	2.5	2.2	3.3	2.5	2.2	2.7	2.9	2.5	3.5	2.3	2.9	3	3	3.1	5.1	4.5	5.2	3.7
Se	ppm	0.1	0.7	0.6	0.8	0.7	0.7	0.7	0.7	0.6	0.8	0.6	0.7	0.7	0.7	0.7	0.6	0.5	0.5	0.7	0.6	0.6	0.6	0.5	0.7	0.5	0.6	0.6	0.7	0.6	0.7	0.7	0.8	0.7	0.6	0.8
Eu	ppm	0.1	0.8	0.7	0.6	0.6	0.8	0.6	0.6	0.5	0.6	0.6	0.6	0.5	0.5	0.6	0.5	0.7	0.5	0.4	0.5	0.4	0.4	0.5	0.6	0.4	0.5	0.4	0.5	0.5	0.6	0.5	0.6	0.9	0.9	0.7
Gd	ppm	0.1	3.7	3.6	2.7	3.3	3.5	2.9	2.8	2.6	3	3.3	2.9	2.7	2.3	3.4	2.5	2.8	2.3	2	2.9	2.3	2	2.4	2.7	2.5	3.1	2.1	2.6	2.7	2.9	2.7	4.6	3.8	4.1	3.1

Tb	ppm	0.1	0.5	0.4	0.4	0.4	0.5	0.4	0.4	0.4	0.4	0.4	0.4	0.4	0.3	0.4	0.3	0.3	0.3	0.3	0.4	0.3	0.3	0.3	0.4	0.3	0.4	0.3	0.3	0.4	0.4	0.3	0.6	0.5	0.5	0.4
Dy	ppm	0.1	2.3	2	1.7	2	2.2	1.9	1.8	1.8	2	1.9	1.6	2	1.5	2	1.5	1.3	1.6	1.2	1.9	1.4	1.5	1.6	1.9	1.6	1.9	1.4	1.7	1.7	1.8	1.6	2.8	2	2	1.8
Ho	ppm	0.1	0.5	0.4	0.4	0.4	0.5	0.4	0.4	0.4	0.5	0.4	0.4	0.5	0.3	0.5	0.3	0.3	0.4	0.3	0.4	0.3	0.3	0.4	0.4	0.4	0.4	0.3	0.4	0.4	0.4	0.3	0.6	0.4	0.4	0.4
Er	ppm	0.1	1.2	1	0.9	1.1	1.3	1.1	1.1	1.1	1.2	1	0.9	1.3	0.8	1.1	0.8	0.7	1	0.7	1.1	0.8	1	1	1.2	0.9	1.1	0.8	1	0.9	1	0.8	1.4	1	0.8	0.9
Tm	ppm	0.1	0.2	0.1	0.1	0.1	0.2	0.1	0.1	0.1	0.2	0.1	0.1	0.2	0.1	0.1	0.1	< 0.1	0.1	< 0.1	0.2	0.1	0.1	0.1	0.2	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.2	0.1	< 0.1	0.1
Yb	ppm	0.1	1	0.8	0.8	0.9	1	0.9	0.9	0.9	1	0.8	0.7	1.2	0.7	0.9	0.7	0.5	0.9	0.6	1	0.6	0.9	0.9	1	0.8	1	0.7	0.8	0.8	0.9	0.7	1.1	0.8	0.5	0.7
Lu	ppm	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.2	< 0.1	0.1	0.1	< 0.1	0.1	< 0.1	0.1	< 0.1	0.1	0.1	0.1	0.1	0.1	< 0.1	0.1	0.1	0.1	< 0.1	0.1	0.1	< 0.1	0.1
Hf	ppm	0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1
Ta	ppm	0.05	< 0.05	< 0.05	< 0.05	< 0.05	< 0.05	< 0.05	< 0.05	< 0.05	< 0.05	< 0.05	< 0.05	< 0.05	< 0.05	< 0.05	< 0.05	< 0.05	< 0.05	< 0.05	< 0.05	< 0.05	< 0.05	< 0.05	< 0.05	< 0.05	< 0.05	< 0.05	< 0.05	< 0.05	< 0.05	< 0.05	< 0.05	< 0.05	< 0.05	< 0.05
W	ppm	0.1	0.2	0.3	0.2	0.5	0.2	0.1	0.2	0.2	0.2	0.3	0.3	12.9	0.4	0.3	0.2	< 0.1	0.3	0.3	0.3	0.4	0.4	0.7	0.4	0.4	0.4	0.4	0.4	0.3	0.3	0.7	0.3	0.1	0.4	0.2
Re	ppm	0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001
Au	ppb	0.5	< 0.5	7	1.7	9.2	22	< 0.5	< 0.5	< 0.5	< 0.5	3.9	19.9	4.6	13.9	2.5	7.7	< 0.5	203	10	17.3	9.5	8.7	17	16.3	< 0.5	< 0.5	9.8	24.7	8.1	5.8	127	< 0.5	< 0.5	< 0.5	30.8
Tl	ppm	0.02	0.39	0.39	0.31	0.33	0.29	0.29	0.24	0.22	0.27	0.33	0.35	0.22	0.29	0.4	0.33	0.15	0.19	0.21	0.34	0.32	0.18	0.24	0.26	0.38	0.35	0.27	0.27	0.33	0.28	0.28	0.29	0.45	0.6	0.37
Pb	ppm	0.01	23.5	29.7	30.4	80.2	56.5	22	22.1	25.2	37.5	24.5	58.5	103	42.9	21.1	32.5	17.9	75.2	43.1	40.5	29.9	289	107	62.1	17.7	21.1	37.9	47	39.6	28.2	89.1	10.7	14.7	12.7	50.1
Th	ppm	0.1	11.3	10	6.5	8.8	8	7	7	6	8	9.3	5.8	4.7	4.5	11	5.4	7.8	4.5	1.9	7.9	5.5	3.3	6.5	7.4	7.3	9.9	6	7.4	7	7.2	7.3	16	11.4	15	8.2
U	ppm	0.1	1.4	1.6	1	1.4	1	1.1	1.3	1	1.1	1.3	1.2	1.2	1.1	1.2	1	0.8	1	0.9	1.3	1.1	0.9	1	1.1	1	1.2	1.1	1.1	1.1	1.1	1.1	1.6	1.4	1.9	1.4
Hg	ppb	10	70	150	150	220	90	20	30	50	80	70	150	100	90	60	80	10	1340	150	150	70	70	80	110	60	50	310	250	110	90	200	20	20	< 10	140